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(54) ACTIVE MATERIAL FOR LITHIUM BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance capacity by constituting an active material of Li, Cu, P and O elements of the specific ratio.

SOLUTION: An active material is expressed by a chemical formula ($LiCu_{1-x}PO_4$). Here, ($0 \leq X \leq 1$) is realized. In this active material, a crystal system is an orthorhombic system in ($0.5<X<1$), and a unit lattice constant of its crystal lattice is ($a=5.31\pm0.5$, and $b=13.43\pm0.5$ and $c=4.91+0.5$) in an angstrom unit. Such an active material is manufactured by heating it in two stages at 450°C, then, at 800°C after pressurizing/molding them into a pellet shape under pressure of 400 kgf/cm2 by mixing them in the stoichiometric ratio of Li_2CO_3, CuO and $(NH_4)_2HPO_4$. A battery is composed of a positive electrode having this active material, an electrolyte and a negative electrode being Li, an Li alloy, Li_xSnO_2, carbon and/or a graphite material. To put it concretely, a battery having high capacity such as 600 mAh/g is obtained.

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[The technical field to which invention belongs] this invention relates to a lithium cell.
[Description of the Prior Art] Many small rechargeable batteries are used as objects for consumer electronic equipment, such as a computer, a camcorder, and a cellular phone, as an important thing as portable power supplies, such as lighting of a tool or a toy. Recently, it has a new interest in the "lithium ion" rechargeable battery which used the intercalation compound which carries out occlusion discharge of the lithium as a negative electrode which changes a lithium secondary battery to a metal lithium. However, in this cell, it is necessary to choose carefully the host substance of a positive electrode and a negative electrode. LiMeO2(Me:Co, nickel) [Mat.Res.Bull.15 (1980) 783 of the layer structure, J.Appl.Phys
19(1980) 305] and a three-dimensions spinel type oxide, and LiMn 2O4 [Mat.Res.Bull.18 (1983) 461, Mat.Res.Bull.19 (1984) 179] -- one half of the times of a charging time value -- a lithium -- receiving -- about 4 -- it has the discharge voltage of V and attention is attracted as a positive active material for lithium ion batteries Recently, it inquires just about the ability of the positive-electrode matter of other kinds to use it for a lithium ion battery. These compounds are similar to Nasicon which consists of LixM2(PO4)3M (Ti, V, Fe) and a three-dimensions skeletal structure like M2(SO4)3(M:Ti, Fe) [Solid State ionic92(1996) 1]. In Japanese JP,9,B -134725, 9-134724, and 9-171827, LiMPO4, M:nickel, and Co, Mn and Cu are indicated by the claim. The matter concerning this invention is a completely different kind, and these matter has olivine structure.
[Problem(s) to be Solved by the Invention] this invention aims at offering a new high capacity active material as an active material for lithium cells.
[Means for Solving the Problem] The active material for lithium cells which becomes this invention is characterized by what is expressed with chemical formula LiCu1+xPO4 (0<=X<=1). 2nd invention concerning the 1st invention is characterized by crystal system being orthorhombic system in 0.5< X<=1. 3rd invention concerning the 2nd invention is characterized by the unit-lattice constants of an orthorhombic-system crystal lattice being a= 5.31**0.5A, b= 13.43**0.5A, and c= 4.91**0.5A. the thing concerning [the 4th invention concerning the 1st to 3rd invention] the manufacture method of the active material for lithium cells -- it is -- Li2 -- it mixes by the stoichiometry-ratio of CO3, CuO, and (NH4) 2HPO4, pressurization molding is carried out by the pressure of 400 kgf/cm2 at the shape of a pellet, and it is characterized by being 450 degrees C and subsequently heating two stages at 800 degrees C 5th invention is characterized by having an active material concerning the 1st, the 2nd, or 3rd invention about the positive electrode for lithium cells. 6th invention is characterized by consisting of negative electrodes which are the positive electrode concerning the 5th invention, the electrolytic solution and Li, Li alloy, LixSnO2, carbon, and/or graphite material about a cell.
[Embodiments of the Invention] Although this invention is explained in full detail based on the gestalt and drawing of 1 operation, it is not limited to this.
LiCu1+xPO4 (0<=X<=0.5) concerning a [example 1] this invention -- Li2 -- it mixed by the stoichiometry-ratio of CO3, CuO, and (NH4) 2HPO4, and prepared by the single step reaction This

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mixture was mashed with the agate mortar, and it was made the pellet by the pressure of 400 kgf/cm2, subsequently calcinated in 450-degree C heating air for 4 hours, and heated at 800 more degrees C for 24 hours. The obtained matter presented blue.
LiCu1+xPO4 (0.5< X<=1) concerning a [example 2] this invention -- Li2 -- it mixed by the stoichiometry-ratio of CO3, CuO, and (NH4) 2HPO4 **, and prepared by the single step reaction This mixture was mashed with the agate mortar, and it was made the pellet by the pressure of 400 kgf/cm2, and subsequently it calcinated in 450-degree C heating air for 4 hours, and heated at 800 degrees C continuously for 24 hours. Consequently, the obtained matter presented green. A of drawing 1 and B show the X diffraction pattern in LiCu1+xPO4, X= 0, and X= 1 concerning this invention. The matter of X= 0 is difficult for there being many peaks and specifying a compound. Since this X diffraction pattern cannot be specified as mixture of the well-known compound containing Li, Cu, and phosphoric acid therefore, the author etc. has judged that it is that in which the matter of this invention has a new chemistry phase. The pattern with the same said of ** was observed by LiCu1+xPO4 of the range of 0<=X<=0.5. However, the X diffraction pattern of the matter of x= 1 can be specified by the orthorhombic-system symmetry, and unit-lattice constants are a= 5.31**0.5A, b= 13.43**0.5A, and c= 4.91**0.5A. The same pattern was observed also in LiCu1+xPO4 of the range of 0.5< X<=1. Drawing 2 shows the cyclic BORUTAN meter of LiCuPO4. This matter shows the single reduction peak to the 2.1V neighborhood without the corresponding oxidization peak. In this case, the trace speed was made into 0.2mV/min. and LiClO4/2EC+2DMC+DEC was used as the electrolytic solution. Drawing 3 shows the cyclic BORUTAN meter of LiCu2PO4. This matter shows the single reduction peak without the corresponding oxidization peak near 1.8 VvsLi/Li+. And another another small reduction peak was observed near 1.2 VvsLi/Li+. In this case, the trace speed was made into 0.2mV/min. and LiClO4/2EC+2DMC+DEC was used as the electrolytic solution. Drawing 4 shows the charge-and-discharge curve concerning the two cycle of the beginning of LiCuPO4 which becomes this invention. This examination made current density 0.1 mA/cm2, and was performed in the glass cell using LiClO4/2EC+2DMC+DEC. This cell consists of a positive electrode (PVDF8% is included 87% [of active materials which become this invention], and carbon black 5%), and the lithium electrode and lithium reference electrode as a counter electrode. First, the cell was discharged and the lithium was inserted in the matter of this invention. This cell shows the flat potential of 2 VvsLi/Li+, and shows the high capacity of 600 mAh/g. The matter with many lithium contents was formed during electric discharge, and this large capacity is ******(ed). Drawing 5 shows the X diffraction pattern of LiCuPO4 after electric discharge. From this drawing, two new phases equivalent to Li3PO4 and metal Cooper were obtained. It is shown that LiCu1+xPO4 (0<=X<=1) decomposes this result into Li3PO4 and metal Cooper with many lithium contents in electric discharge process. Therefore, it is thought that the large service capacity observed by this matter is based on the generation of Li3PO4 with many lithium contents. Drawing 6 shows the Cu2pXPS spectrum of LiCuPO4 before and after electric discharge. A peak is shifted to the low 932.5eV binding energy side which shows metal Cooper's property after electric discharge. It checked that metal Cooper existed by this in LiCuPO4 which discharged.
[Effect of the Invention] About the new active material this invention is indicated to be by chemical formula LiCu1+xPO4 (0<=X<=1), this matter has the crystal structure which changed with X values, and its capacity is as high as 600 mAh/g, and it can use it as a positive active material of the lithium primary cell whose voltage is 2VvsLi/Li+.

[Translation done.]